Development of an Atmospheric Mercury Modeling System for the Great Lakes Region

Progress Report for the Quarterly Period Ending June 30, 2002

Wisconsin Department of Natural Resources
Mercury Analysis Team

The Mercury Analysis Team, part of the Wisconsin Department of Natural Resources' (DNR) Air Management Program, is responsible for developing an atmospheric mercury modeling system for Wisconsin and the Great Lakes region. Partial funding for this effort comes from a grant awarded by USEPA in October 2001. The team identified seven major areas of work and the lead staff for each as follows:

- Atmospheric Chemistry Modeling, Mike Majewski – WDNR
- Meteorological Modeling, Wusheng Ji – WDNR
- Regional Emission Modeling, Gwendolyn Judson – WDNR
- Mercury Inventory Development, Orlando Cabrera-Rivera & Grant Hetherington – WDNR
- Data Analyses, William Adamski, Grace Liu & Sanober Durrani – WDNR
- Mercury Monitoring, Mark Allen – WDNR
- Computer Resources, Mike Majewski – WDNR

Initially, all our modeling has been based on the modeling performed by SAI for LADCO using REMSAD. For the next phase of effort, the Team has decided to work cooperatively with the PM and haze modeling being done by LADCO. Using the same modeling domain and episodes will allow us to use their data for the particulate and ozone inputs, allowing us to focus on the mercury component. This transition should occur in the next several months, as soon as a full set of data becomes available.

The Team meets on a regular basis and is the coordinating body for this project providing staff and other interested parties the opportunity to contribute feedback and ideas. Meeting minutes can be found at www.dnr.state.wi.us/org/aw/air/staff/hganalysisteam/index.htm. This document records our progress in each major area for the quarter ending June 31, 2002.

Atmospheric Chemistry Modeling

Presently, the chemistry model being used is the Regional Modeling System for Aerosols and Deposition (REMSAD) version 6.2. The REMSAD modeling system was developed for the Lake Michigan Air Directors Consortium (LADCO) by Systems Applications International (SAI), a part of ICF Consulting. Recently, version 6.4 of REMSAD became available.

The modeling tasks were divided into four sections. The first task was to complete some "practice" modeling. Second, run simple sensitivity tasks to determine the response of the model to changes in some input. Third, perform basecase modeling and evaluate model performance. Fourth, examine some emissions control strategies that may be effective in reducing the deposition of mercury to water bodies in the Great Lakes region.

The primary modeling work so far has been completing tasks one and two. All work has been done using the data set developed by SAI in their mercury modeling work for LADCO. Namely, all meteorological and emissions data were for the year 1996.

Practice modeling

Loading the REMSAD model code on to our DEC workstation and compiling it was completed without problems. The model was run for the month of January 1996. This output was then compared to data sent by SAI for the month of January. Wisconsin DNR results compared very favorably with those from SAI. Maximum difference plots between the SAI and DNR runs yielded no differences.

Sensitivity Tests

The first sensitivity tests investigated the importance of the surface chlorine concentration file. This file is only used in the mercury chemistry routine. A chlorine concentration value is needed for every cell in the coarse grid. The current REMSAD User's Guide recommendation is a value of 125 ppt over the ocean and up to 100-km inland. Over land, the recommendation is 5 ppt. Three tests were done with the surface chlorine concentration file. First, over land concentrations were increased from 5 to 15 ppt. Second, over water concentrations were reduced from 125 ppt to 65 ppt. Finally, over land concentrations were increased from 5 to 1000 ppt. These test were initially were run for the month of January. Difference plots between the sensitivity tests and the January basecase revealed no significant differences.

The tests were repeated for the "warm" month of July. After establishing the base level values for July, the three sensitivity tests were completed. Again, there were no significant differences. These results are somewhat puzzling because the equations for the mercury reactions involve chlorine and significant changes were made to the chlorine levels. This surface chlorine concentration file appears to be the only source of chlorine in the model. Some larger differences were expected from these changes. Figure 1 is a typical difference plot for tests involving the surface chlorine concentration file.

The fourth sensitivity test involved setting the boundary conditions for the various mercury species to zero. This would give us an idea of the impact of the boundary conditions on mercury deposition. As expected the maximum difference plots indicated greatest changes in deposition occur along the modeling domain boundaries (Figure 2). Mercury reduction over Wisconsin is about 1 gr/km^2 with some 1-2 gr/km^2 along the western lake Michigan shore. Mercury deposition, in the basecase run, was 1-2 gr/km^2. Thus, most of the deposition over Wisconsin appears to be due to the boundary conditions. Although the contribution of the boundary conditions may be correct, the amount of deposition predicted in the basecase may be too small. This results in the boundary values having a disproportionately large effect. Or, in other words, local emissions of mercury have almost no impact on the mercury deposition in the state.

The fifth sensitivity test involved increasing the mercury emissions from the elevated point sources in the modeling domain by a factor of 5. This was an attempt to increase the amount of mercury that would be available for deposition in northern Wisconsin. Maximum total mercury deposition in the modeling domain increased from 46 gr/km^2 to 152 gr/km^2. Although there are large differences (max. difference of 120 gr/km^2 near Detroit) they tend to occur very close to the source (Figure 3). It appears the mercury does not travel very far from the source before it is deposited. Differences in northern Wisconsin between the basecase and this sensitivity test are about 1 gr/km^2 or less.

For the next test, mercury emissions from low-level area sources within the fine grid domain were increased by a factor of 5. Maximum total mercury deposition increased from 47 gr/km^2 to 230 gr/km^2. Deposition difference plots (Figure 4) indicate the area source emissions also have minimal dispersion. The deposition is occurring relatively close to the source. As with elevated point sources, there is little deposition in northern Wisconsin from the low-level area sources. The seventh sensitivity test involved setting the rainfall rates to zero throughout the domain. Difference plots of wet deposition indicated a decrease in deposition of 9.4 gr/km^2 in the Detroit area. This is the location and magnitude of maximum wet deposition in the basecase run. Thus, this is not an unexpected result. There were no locations where mercury deposition increased by removing the precipitation.

Current Work

As mentioned above, REMSAD version 6.4 is now available to us. We are re-running the basecase emissions for the month of July. However, we have encountered some errors that caused the job to stop running. SAI has provided some new source code that has allowed the mercury job to continue running past the trouble spot. Results will be compared with version 6.2 output to see if any differences exist. Version 6.4 results will also be compared to observed values for the month of July. Subsequent mercury modeling will be performed with the version that performs best.

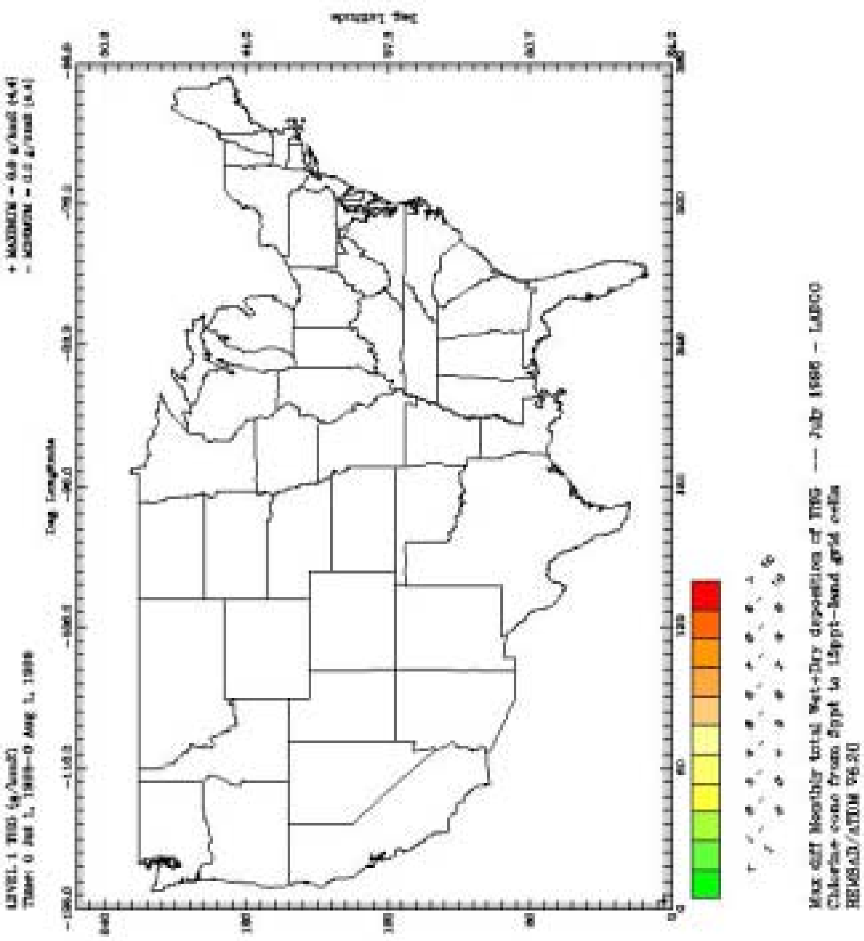

Figure 1: Typical difference plot for tests involving the surface chlorine concentration file.

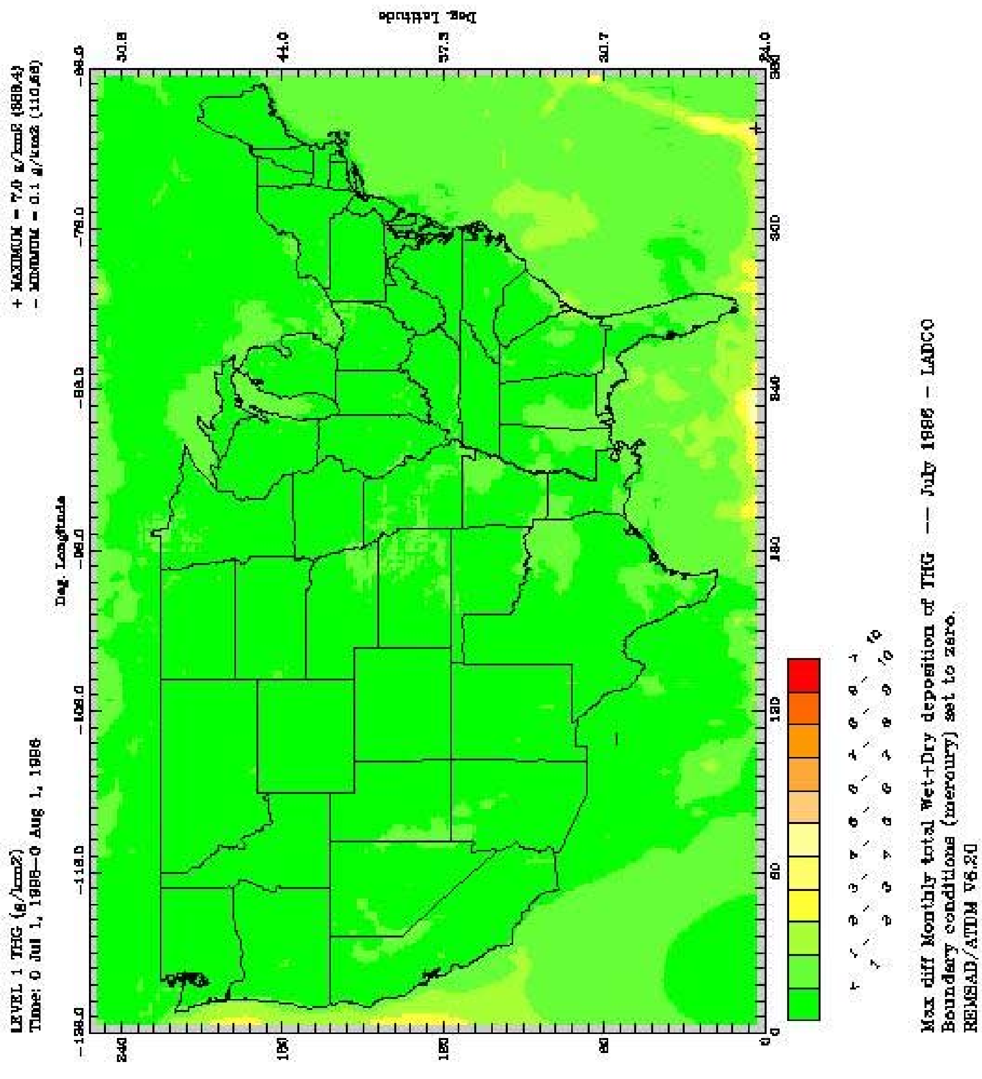

Figure 2: Maximum difference plot from boundary condition sensitivity test.

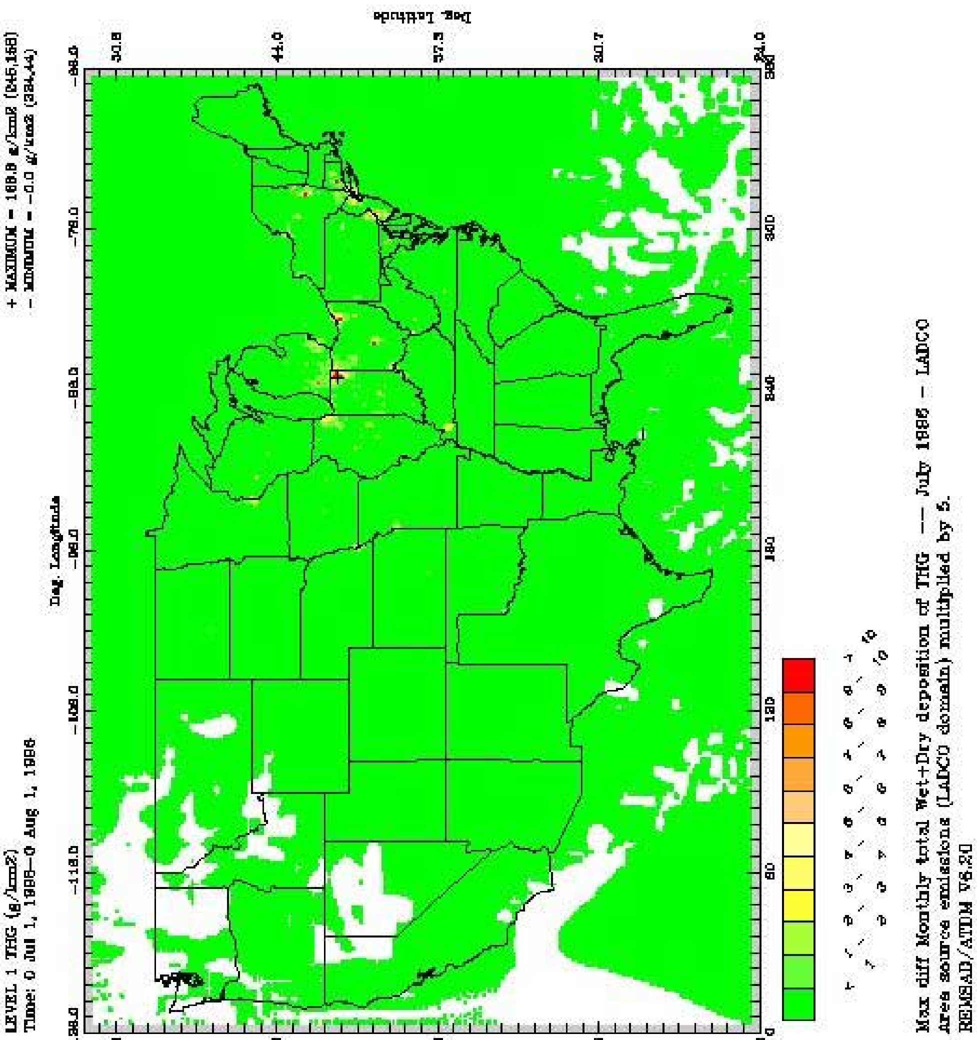

Figure 3: Maximum difference plot from elevated point source sensitivity test.

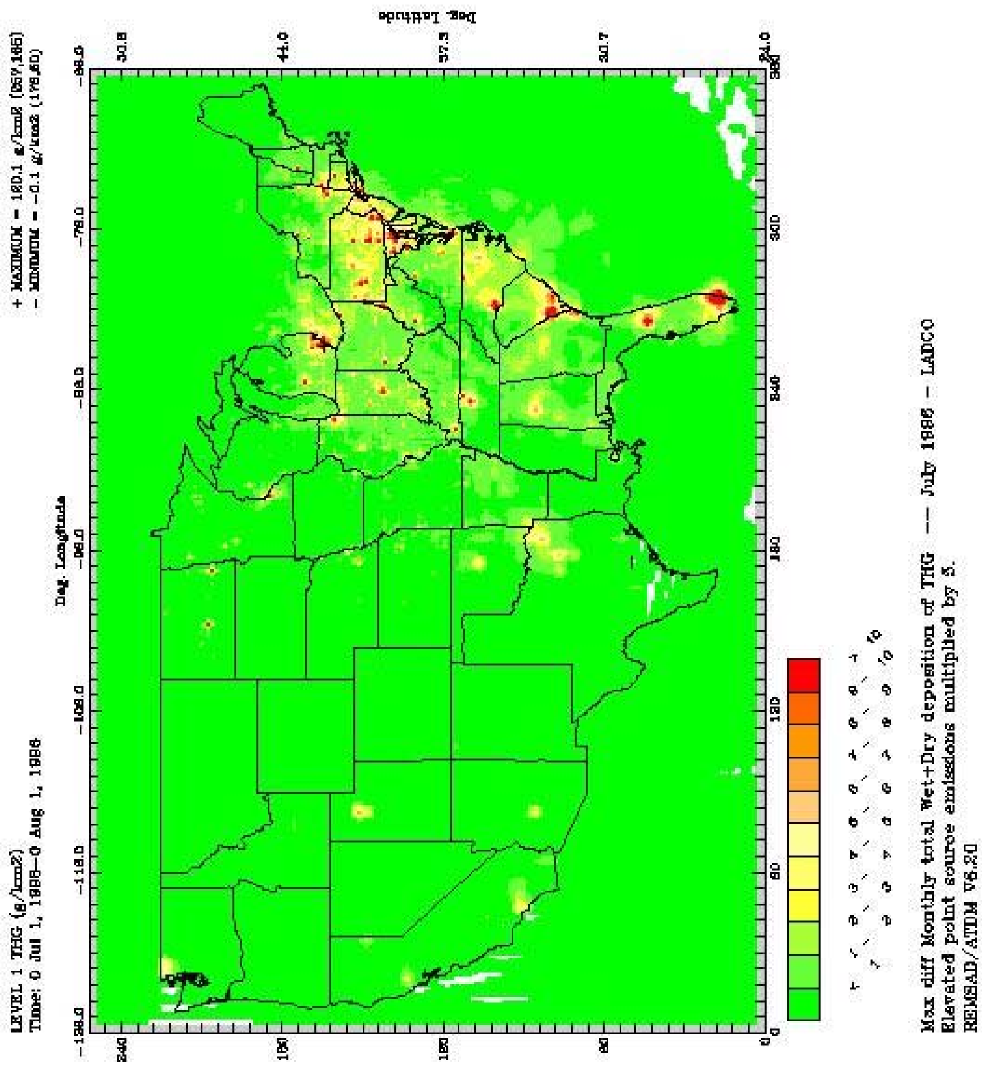

Figure 4: Maximum difference plot from low-level area source sensitivity test.

Meteorological Modeling

The Team has identified three possible episodes to use for evaluating mercury deposition during rainfall events: June 23-29, 1998; June 1-7, 1999; and June 29-July 5, 1999. The episode of June 23-29, 1998, was chosen for the initial run and evaluation of performance.

June 23-29, 1998, was a seven-day episode with the synoptic feature being a major east-west stationary frontal band that remained over the Midwest. This resulted in some severe mesoscale convection and considerable precipitation over Wisconsin, as shown by Fig. 5 of NOAA 1200 UTC map for June 26, 1998.

In order to recreate the meteorology input for the mercury modeling, the Fifth-Generation Penn State/NCAR Mesoscale Modeling System (MM5) was selected to simulate the meteorology conditions for the episode since it is a widely utilized and well-developed prognostic mesoscale model. The model was configured as a three-dimensional, non-hydrostatic model capable of fully simulating the mesoscale perturbations and precipitation induced by the stationary front within the context of a non-stationary synoptic environment. MM5's nested grid interactive feature was used with two horizontal grids of 36km and 12km as shown by Fig. 6, respectively. The coarse, national scale 36km grid had 149X99 grid points with the domain centered over Wisconsin and covered most of the contiguous U.S. and portion of Canada. The inner 12km grid had 166X163 grid points and covered in an area from Texas at southwest corner, South Carolina at southeast, Saskatchewan at northwest and Quebec at northeast. Both grids employed 41 layers with a 116 m vertical spacing in the lowest level, gradually stretching upward to about 688 m by the top level near 17km. The atmospheric data used for initializing the MM5 simulations as well as in the lateral boundary and 4DDDA nudging schemes were analyzed with the NMC 2.5 mandatory level analysis and the conventional surface and upper air data sets obtained from the archives of the National Center for Atmospheric Research. Only the standard NWS rawinsondes at 0000 UTC and 1200 UTC were used in the nudging procedures. Due to dominated synoptic features of a long-lasting stationary front and persistent precipitation during the episode, the explicit cloud and precipitation options were all turned into actives. The explicit moisture schemes with simple ice, Grell cumulus parameterization, high-resolution Blackadar PBL scheme and cloud radiation scheme were employed for this application. The model simulation run starts at 1200UTC on June 21, 1998, ends at 1200UTC on June 30, 1998 with a restarting at 1200UTC on June 25, 1998, and takes about 30 days to simulate the episode on a DEC Alpha workstation.

The model initial results showed that the model had basically produced reasonably well meteorological flow fields and precipitation patterns in simulating the major frontal features affecting Wisconsin, as well as the mesoscale convection associated with the stationary front, as illustrated by figures of Fig. 7 through Fig. 10. At 1300UTC of June 25, the Midwest and Upper Great Lakes were dominated by a low pressure centered over upper Michigan, with a stationary front lay across from Oklahoma through Wisconsin to the low center over Upper Peninsula of Michigan. A frontal rainfall band was moving along the frontal line advancing northeasterly as shown by Fig. 7, along with a secondary rainfall band developing over northern Minnesota. The hourly precipitation produced by the model also displayed a very similar pattern, as shown by Fig. 8. Both maps indicate that there was a front-induced rainfall band extended from Oklahoma through Iowa and then to Wisconsin, with a secondary rainfall region over Minnesota. However, because of an unusual mesoscale disturbance of lower troposphere and highly ageostrophic surface winds over the low center, the debris rainfall patterns displayed by the model over the east side of Lake Michigan near the low center cover an unreasonably large area and are obviously unreal.

Again, Figs. 9 and 10 show the maps of radar reflectivity and hourly rainfall amount respectively. They indicate the model had adequately reproduced the front-induced rainfall area and the developing stage, both showed that a northwest-southeast rainfall band lay across over portions of Minnesota and Wisconsin with a larger area in the middle of the band. Because of the fine grid boundary influence, the modeling again had displayed an unusual rainfall patterns over Manitoba around the grid northwest corner.

It should be emphasized that this report was written with insufficient rainfall observations, and the quantitative analysis of model results remains a problem, whose solution is essential for improvement of the model simulation. This is only a preliminary result of our MM5 modeling; definitely more experiments with better observations are still needed in the future. We may also have to use a finer nested grid to better represent the frontal systems and the mesoscale convection systems associated with them, introduce a more objective way to verify the rainfall amount, and apply a variety of statistical measures to the model results to evaluate them more scientifically.

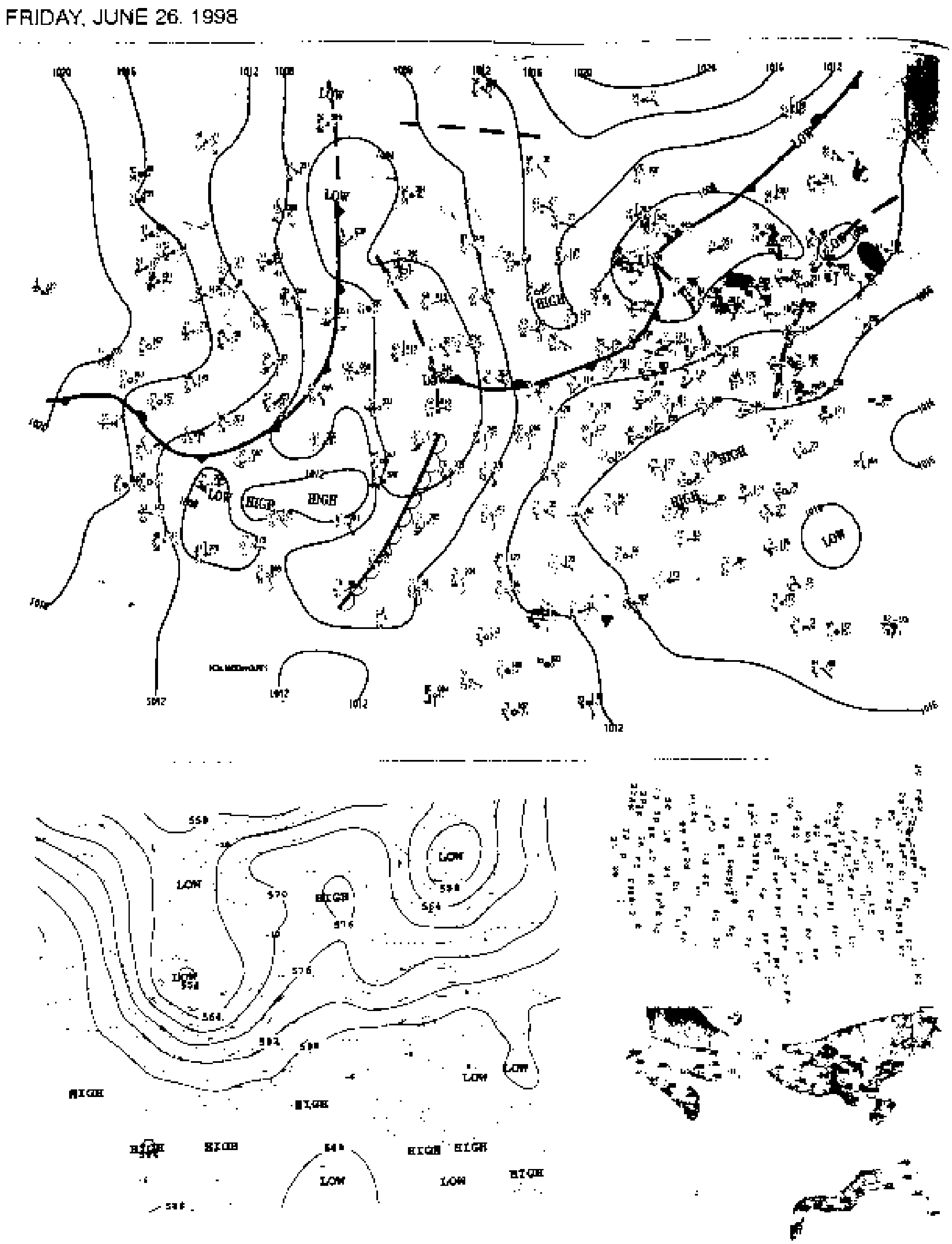

Figure 5: NOAA daily weather maps for June 26, 1998

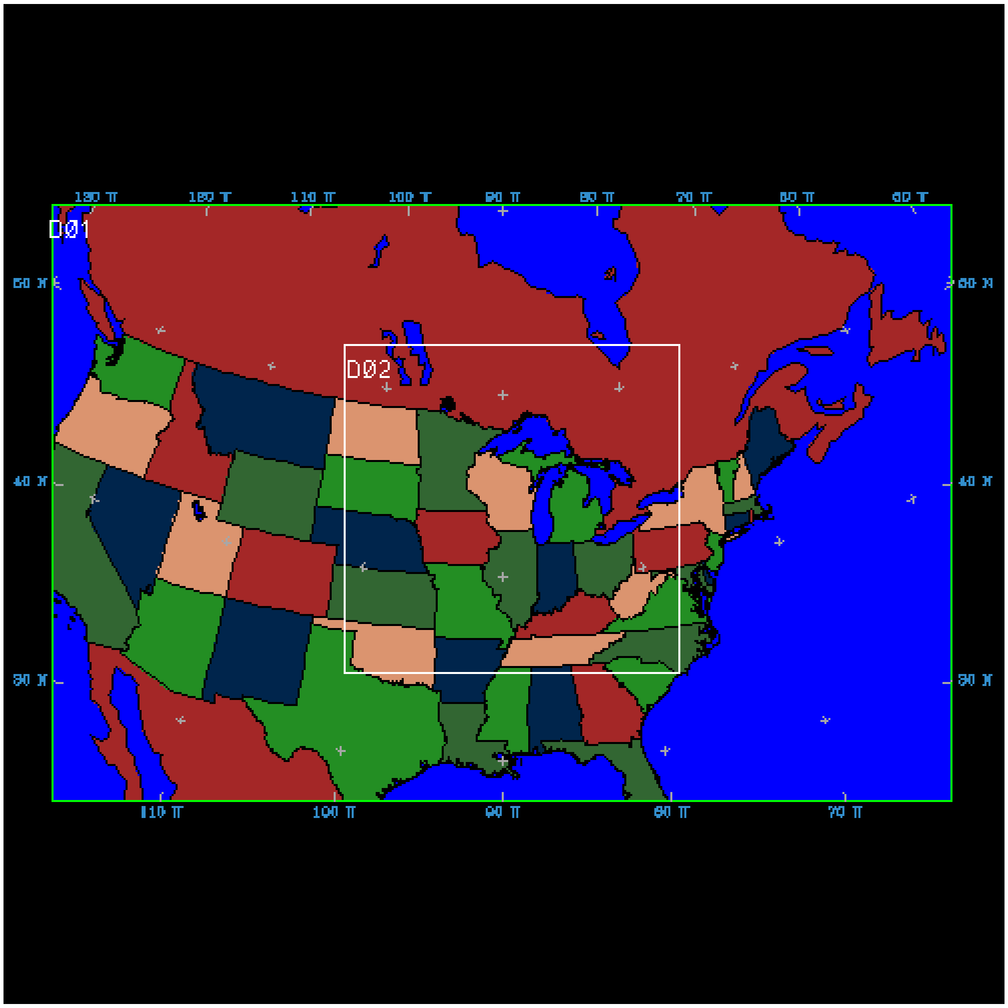

Figure 6: The MM5 modeling domains for June 1998 episode showing the national 36km grid and the inner 12km grid with the grid centers over Wisconsin.

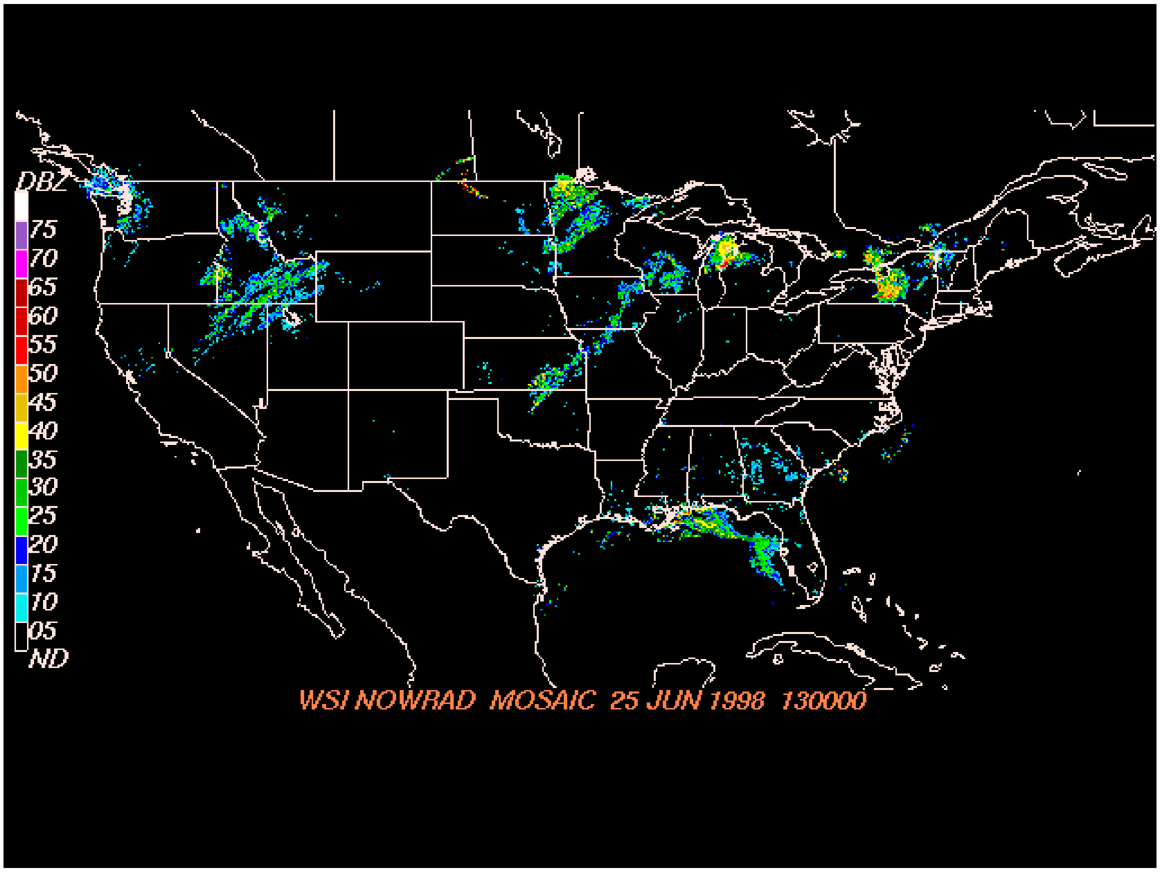

Figure 7: National Mosaic Reflectivity Images for 1300 UTC 25 June 1998.

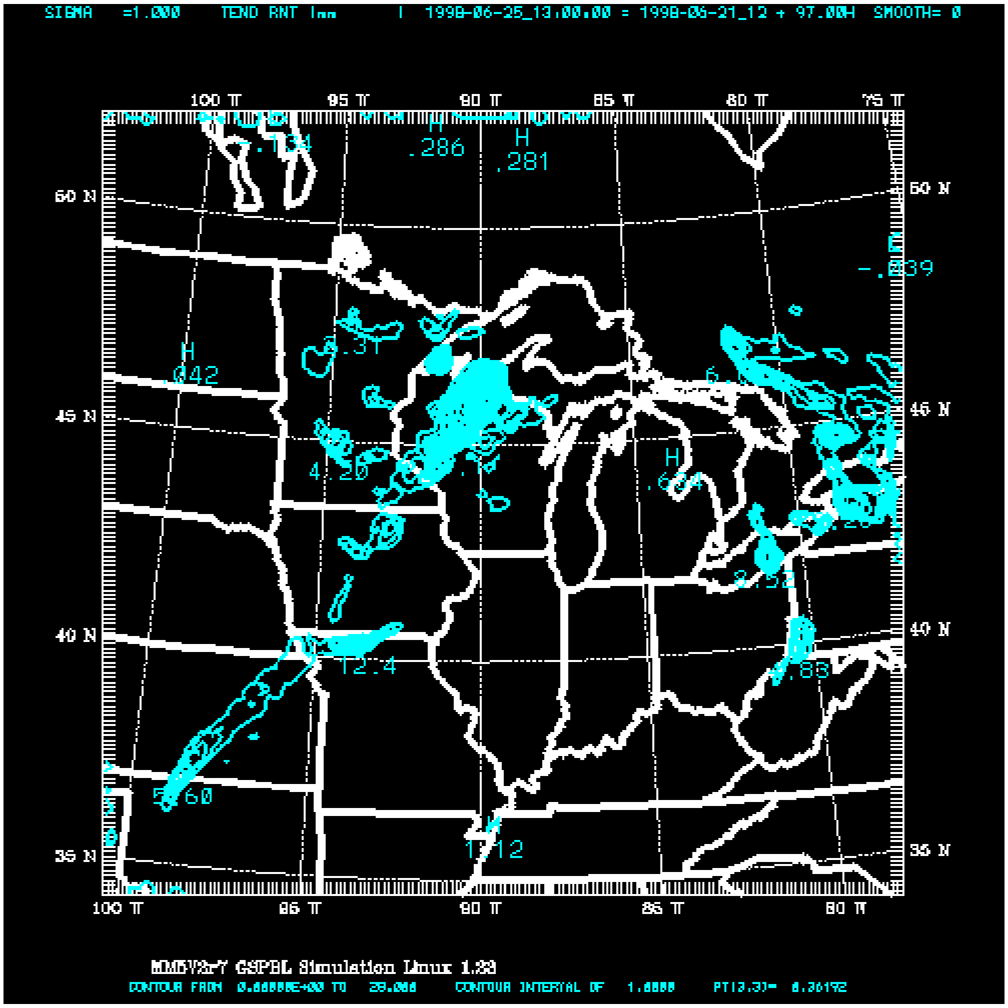

Figure 8: MM5-generated hourly precipitation in the unit of millimeter during the front-induced rainfall of June 25, 1998 at 1300UTC.

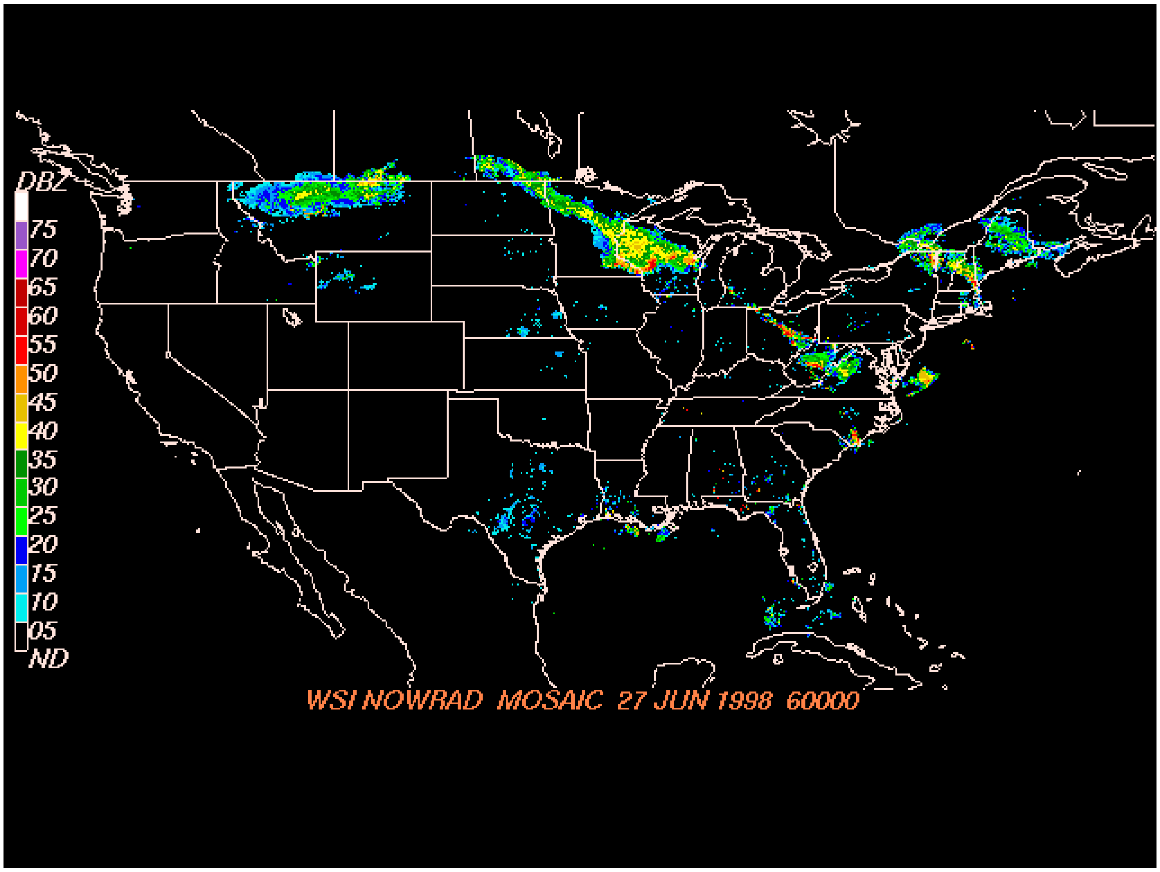

Figure 9: National Mosaic Reflectivity Images for 600 UTC 27 June 1998.

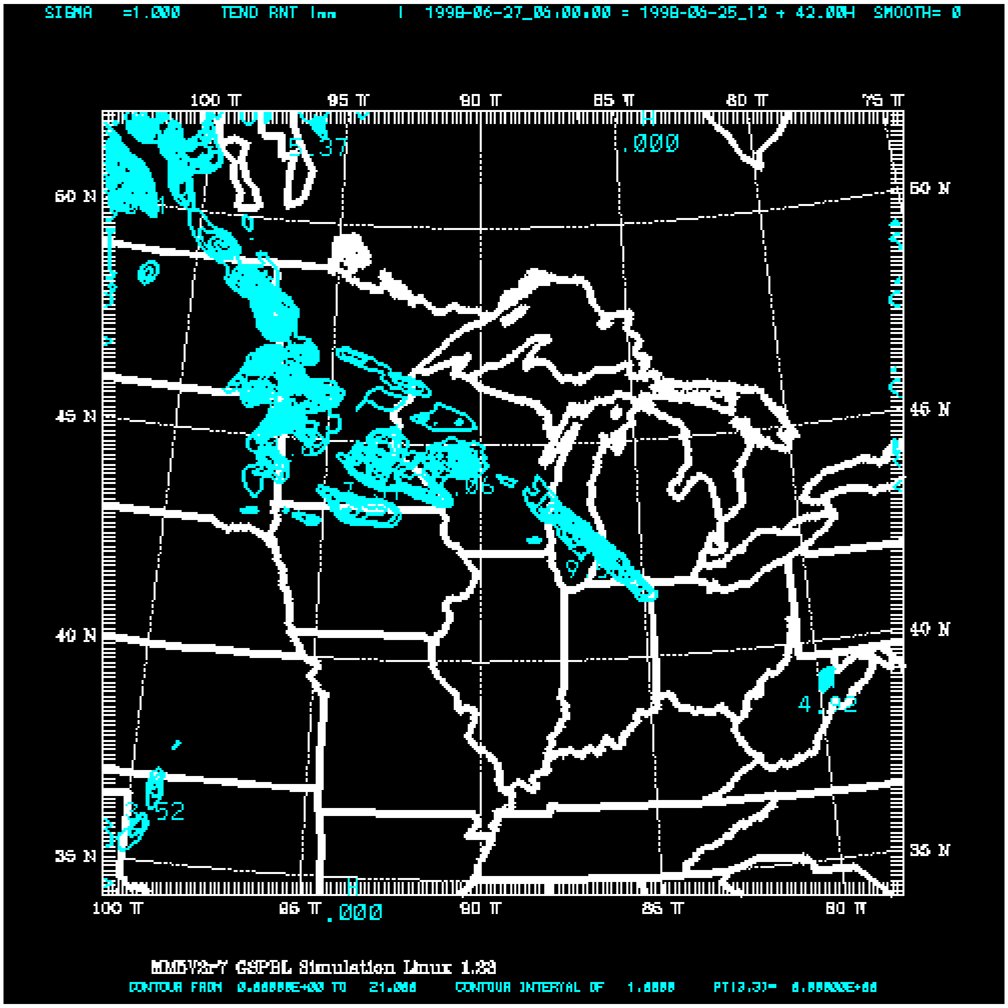

Figure 10: MM5-generated hourly precipitation in the unit of millimeter during the front-induced rainfall of June 27, 1998 at 600UTC.

Regional Emissions Modeling

Regional emissions modeling for this project will be performed using EMS-2001. The National Emission Inventory (NEI) for 1999 will be released in NIF version 2.0. The point and area source processors of EMS-2001 were re-written to match this input format and the data structure of the NEI. These processors are being beta-tested at LADCO as part of their effort to model PM-2.5 and haze.

The draft versions of the 1999 NEI have been run through the QA processors included in EMS-2001. Many critical errors were found. USEPA has indicated that they are working on fixing most of these problems before the next release.

Inventory Development

Last summer (2001), a survey was conducted of twenty-one air pollution state, municipal, and county agencies in eighteen states to gather emission inventory data related to mercury emissions. Most agencies referred us to their latest National Emission Inventory (NEI) submission. A few agencies responded by submitting data. However, typically, the submitted data was either too general or too incomplete to be helpful.

Mercury emissions data from non-point area and mobile sources were compiled. These estimates are part of the Wisconsin portion of the Great Lakes Regional Air Toxic Emissions Inventory Project. The emissions data include crematories, residential fuel combustion, landfills and locomotives.

A draft quality assurance/quality control (QA/QC) plan has been crafted. As part of the QA/QC plan, a draft data processing procedure has been developed incorporating the use of Regional Air Pollutant Inventory Development System (RAPIDS), MS-ACCESS and Emissions Modeling System (EMS) 2001. As the mercury modeling project continues, these products will evolve to include additional relevant parameters of the emission inventory (EI); and to expand QA/QC to more aspects of the most important EI parameters. A preliminary review of mercury data in the March, 2002 release of version 2.0 of the National Emission Inventory (NEI) has been performed. Additionally, a report comparing and evaluating the speciation profiles used in the 1997 Report to Congress, USEPA's draft mercury inventory for 1999, and the 1996 inventory prepared by SAI for the LADCO modeling contract was prepared.

The latest release version 2 of the NEI is due for release in 6/2002. Upon its release, the implementation of the QA/QC plan will begin as the development and refinement of the QA/QC plan continues. One of the first steps will be to compare data submitted to the NEI to Great Lakes States (GLS) data and any data submitted in response to last summer's survey.

Data Analyses

<u>Mercury Monitoring Data Archiving and Analysis</u>

Data that are collected from five Mercury Deposition Network (MDN) sites in Wisconsin have been retrieved, formatted, archived. A preliminary analysis of weekly Hg wet precipitation has been completed. These efforts have been folded into previous work on the MDN database. The overall MDN data analyses have helped identify which time periods should be modeled, as well as establishing a general relationship between rainfall totals and Hg wet deposition and noting seasonal and geographical variations in the overall deposition rates.

Each seven day MDN precipitation sample is measured for total precipitation (liquid water equivalent, units: millimeters [mm]) and non-water soluble gaseous elemental Hg ("wet precipitation Hg", units: nanograms Hg per liter of rainfall [ng/l]). These two measured quantities are multiplied to derive each site-week's wet Hg deposition concentration (units: ng/m^2).

Table 1 contains a summary of the averages of these weekly quantities for each Wisconsin MDN site since the MDN program commenced in 1995.

Wis MDN Site	Ave Measured Weekly Rainfall (mm)	Ave. Measured Weekly Precip. Hg (ng/l)	Ave Calc. Weekly Hg Wet Dep. (ng/m^2)
Brule River	14.85	14.77	177.52
Popple River	12.48	12.37	139.12
Trout Lake	15.02	11.61	166.48
Lake Geneva	8.52	16.53	117.29

Table 1: Average of weekly measurements and derived mercury wet deposition for each Wisconsin MDN site, 1995 – June 2001.

The MDN site at Lake Geneva measured the highest average precipitation Hg totals. Focusing on this MDN site, there appears to be no discernible relationship between weekly rainfall rates and amount of water-soluble gaseous elemental Hg, which is displayed in the following graph:

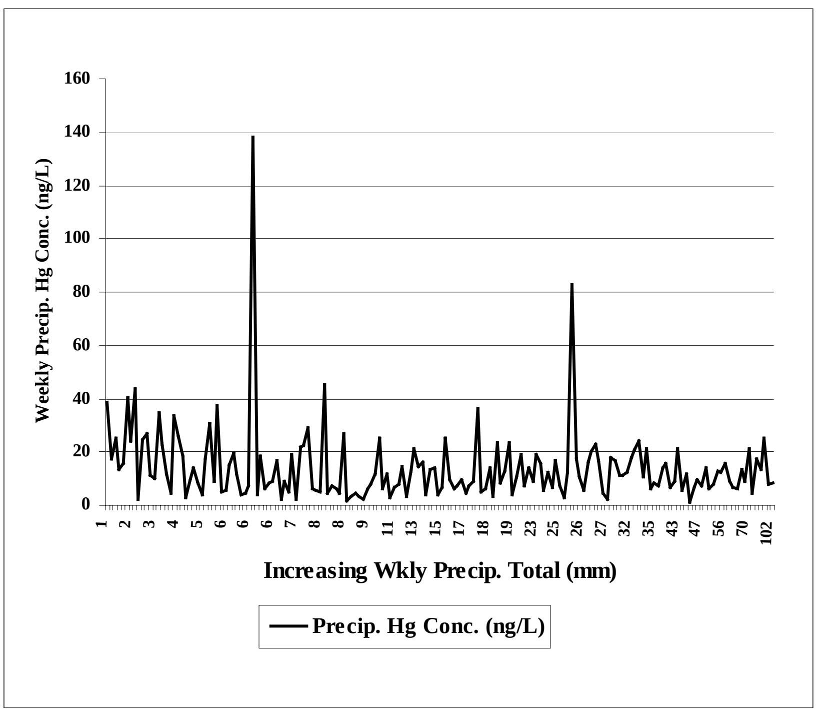

Figure 11: Weekly measured precipitation Hg conc. vs. increasing measured weekly precipitation, Lake Geneva MDN site, Dec 1996 – June 2001.

The average site-weekly precipitation total and wet precipitation Hg amount are multiplied to derive that site-week's Hg wet deposition total. Again employing data from the Lake Geneva MDN site, there appears to a generally proportional relationship between increasing rainfall amounts and by the site's weekly Hg wet deposition rates (Figure 12). This feature is not unexpected since measured rainfall is a factor in deriving Hg wet deposition rates.

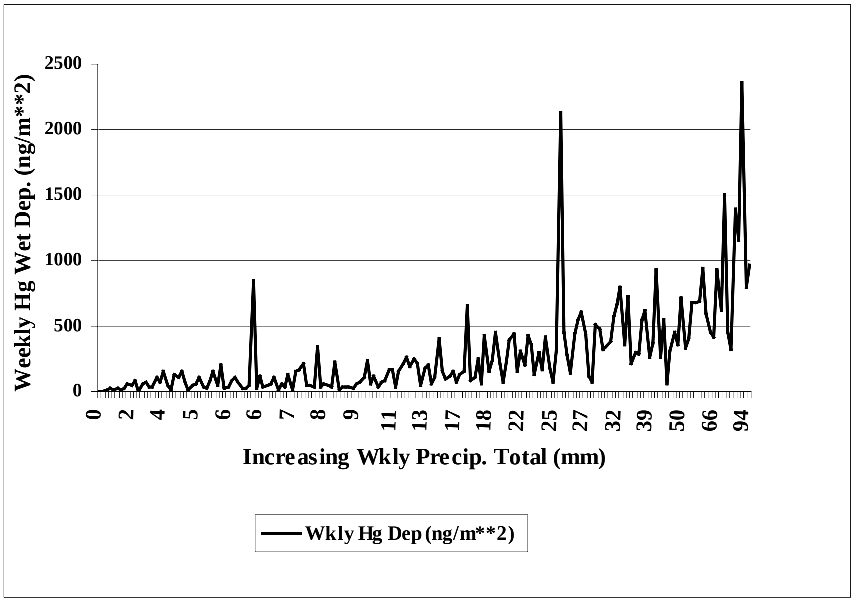

Figure 12: Derived weekly Hg wet deposition rates vs. increasing measured weekly precipitation totals, Lake Geneva MDN site, Dec 1996 – June 2001

Analysis of the Wisconsin MDN data revealed wide variability both among the sites and at individual sites for the measurements collected. However, there was a seasonal trend identified among all the sites. Specifically, noticeably much higher wet precipitation Hg and Hg wet deposition values occurred during Wisconsin's relatively "warm" months (i.e., mid-April to mid-October) than during the "colder" period (i.e., mid-Oct to mid-April) of a typical Wisconsin year (Figures 13 and 14).

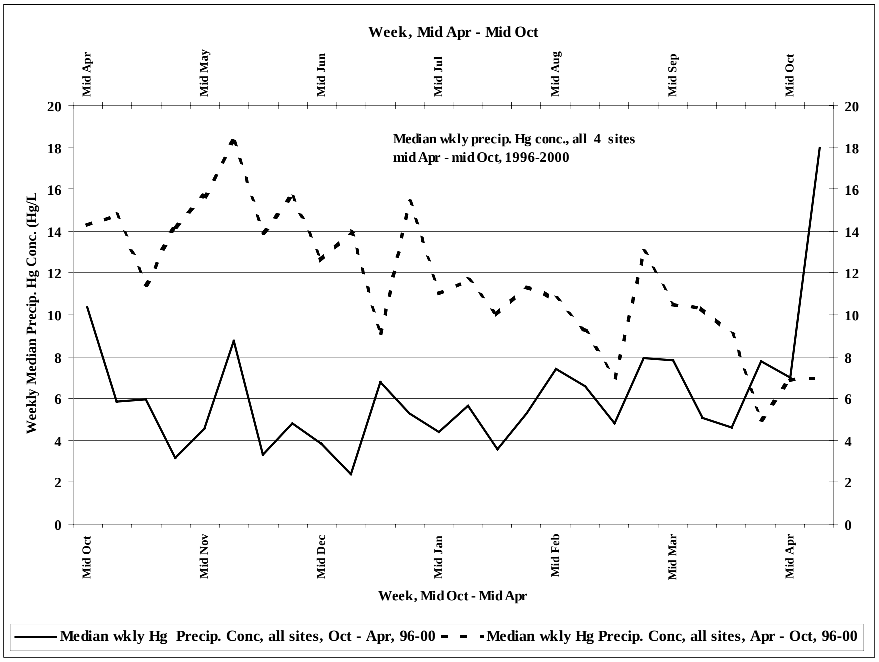

Figure 13: Weekly median precipitation Hg concentrations, All four Wisconsin MDN sites, 26 week periods (mid April – mid Oct, mid-Oct – mid April) 1996 – 2000.

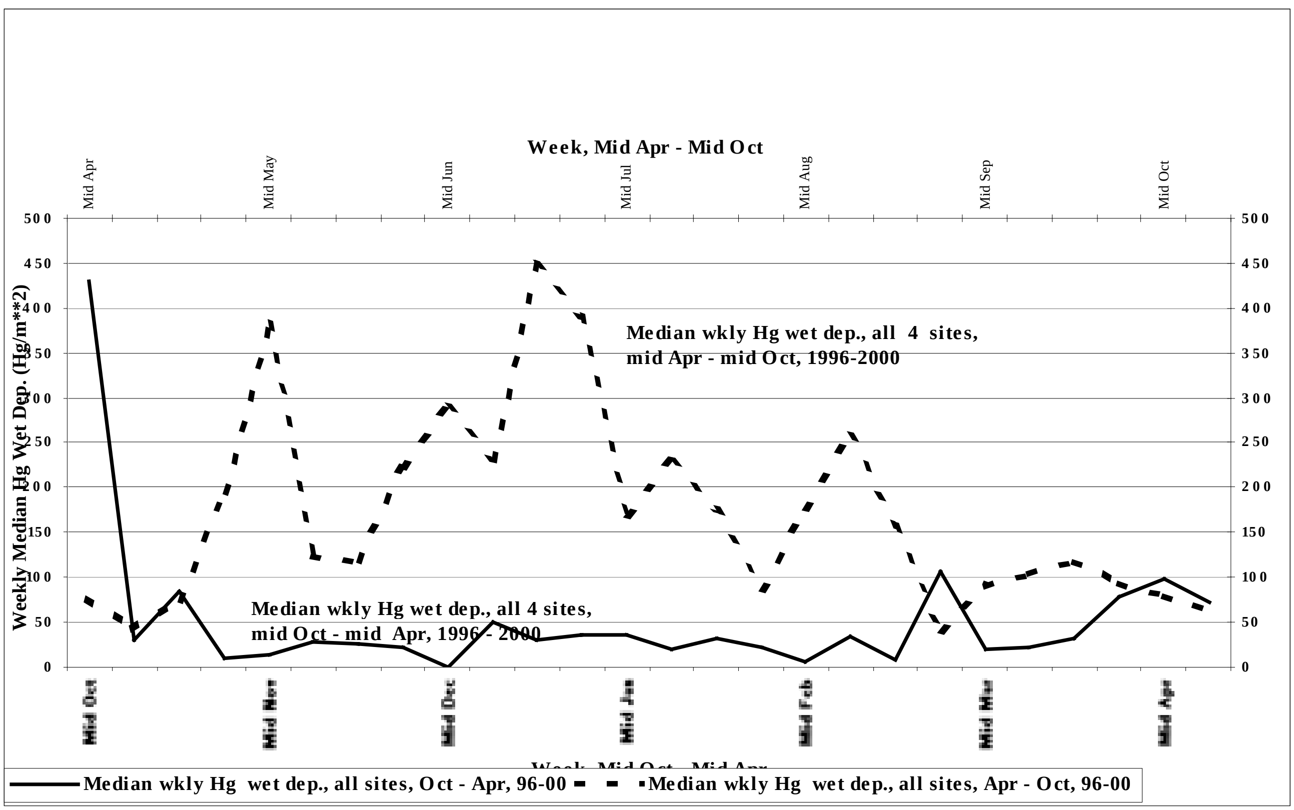

Figure 14: Weekly median Hg deposition rates, All four Wisconsin MDN sites, 26 week periods (mid April – mid Oct, mid-Oct – mid April) 1996 – 2000.

Review, Synthesize and Report on Published Scientific Research

Papers and reports on the science of atmospheric Hg transport and transformation processes continue to be reviewed. These reviews help build on the knowledge that we have to date.

Proposed Mercury Projects

The need to get more ambient monitoring Hg has led to the writing of three proposals in 2002 that seek funding for Hg dry deposition field studies. One proposal was not selected. As of mid-June 2002, we are still waiting for a decision on the other 2 proposals.

Professor Jamie Schauer of the University of Wisconsin was recently awarded funding to conduct a large dry Hg field study in the Devils Lake area. Bill Adamski will help analyze the data collected from this study, which will commence in September.

Chlorine-Mercury Project

Grace Liu and Sanober Durrani are conducting a chlorine-mercury project. The project objective is: "To find out the significance of anthropogenic chlorine in point source mercury chemistry. Model simulations of chlorine-mercury plume chemistry from coal-fired power plants."

After review and evaluation of several emission models; which included ISCST3 dispersion model, Plume-in-Grid (PiG) model, PARADE reactive plume model, and Reactive and Optics Model of Emissions (ROME); ROME was chosen for use to simulate the chlorine-mercury chemistry emitted from specific point sources.

Grace and Sanober summarized the identified transformation pathways of atmospheric mercury as

- Oxidation of elemental mercury with ozone (O_3), gas phase and aqueous phase;
- Oxidation of elemental mercury with chlorine (Cl_2, HOCl, and OCl^-), gas phase and aqueous phase;
- Oxidation of elemental mercury by hydroxyl radicals ($^\bullet OH$), aqueous phase;
- Reduction of divalent mercury by sulfite (SO_3^{2-}) ions, aqueous phase;
- Complexion of divalent mercury with soot to form particulate divalent mercury.

They also adapted the mercury speciation that is mostly employed in many mercury modeling:

- Elemental mercury (Hg^0)
- Divalent mercury (Hg^{2+})
- Particular mercury (Hg_p)

The are considering the following sources to be hypothetical sources in their simulation:

- Manitowoc Public Utilities (FID 436035930)
- Wis DOA/ UW Madison – Charter Street (FID 113008390)
- Appleton Coated L.L.C. (FID 445031290)
- Fort James Operation Company (FID 405032870)
- Stora Enso No. America-Niagara Mill (FID 438039360)

Grace and Sanober will determine at least one hypothetical source that can be applied to our mercury chemistry simulation. At the same time, we will start to explore appropriate mercury monitoring sites in order to validate our future model performance with measured data.

Mercury Monitoring

The 2002 second calendar quarter was a very active period for mercury monitoring in the Wisconsin. Deposition monitoring continued at five mercury deposition sites located in Wisconsin. In addition, ambient monitoring was conducted using three different monitoring techniques. A summary of the monitoring projects follows.

Deposition Monitoring

Wisconsin has five monitoring stations as part of the National Mercury Deposition Network (MDN) operated by the National Atmospheric Deposition Program (NADP). The sites are located at Brule River, Trout Lake, Lake Du Bay, Devils Lake, and Lake Geneva. Four of these sites collect weekly wet deposition samples. A fifth site, at Devils Lake, is operated as an event site where the sample is removed from the collector after each rainfall event. Information about the mercury deposition program as well as historical data for the Wisconsin monitoring stations can be found at the National Atmospheric Deposition Programs web site (http://nadp.sws.uiuc.edu/).

Ambient Monitoring

Mercury surveys continued using the portable LUMEX analyzer. This real time analyzer uses spectrophotometric principles to measure mercury in the air. The LUMEX has both a quick response and high sensitivity with a detection limit of 2 ng/m3 of air. The analyzer is subject to periodic baseline drift that limits its usefulness for long-term unattended operations. A number of surveys were conducted in March and April and these surveys are summarized in David Grande's April 18, 2002 memorandum to Tom Sheffy. Two significant items were David's survey near a neon sign manufacturer in Madison and tests of the instrument during an aircraft flight. The survey near the neon sign manufacturer did not detect mercury in the ambient air. This result should not be taken as an indication that all neon sign manufacturing is mercury free but does indicate that in this survey the facility did not have measurable mercury emissions. The aircraft flight test was designed to test the LUMEX as a portable instrument for monitoring mercury in the ambient air. The aircraft test of the LUMEX showed that spikes could be detected when the flight path passed through a power plant plume. Unfortunately the concentration in the surrounding air were below concentration that could be confidently measured with the LUMEX. The LUMEX would not be useful for general monitoring from an aircraft platform.

The Mercury Analysis Trailer (MAT) shared with Michigan and Minnesota was available to the WDNR from mid-March until the end of May. The MAT contains two TEKRAN 2537a analyzers and supporting equipment. During this time the monitoring staff conducted tests of the TEKRAN equipment and conducted a number of monitoring projects. The most significant monitoring project was conducted from April 4 through May 16 at the Mercury Waste Solutions facility located in Union Grove. Mercury Waste Solution Inc. is a large mercury recycling company and the Union Grove is the national processing center for the company. With the cooperation of the facility, the MAT was placed on the facility's property and the ambient air measured continuously for 44 days. The second TEKRAN analyzer was used for studies at other two Wisconsin monitoring sites. The first site was located in a trailer near the Vulcan chemical plant in Port Edwards. Vulcan Chemical is the only chlor-akyl plant in Wisconsin using mercury filled cells. The second site used was at the Madison ozone monitoring station where the analyzer tested urban air. At the completion of the monitoring in Union Grove the Trailer with both analyzers was moved to the Nevin Fish Hatchery in Madison. The Nevin Fish Hatchery has a relatively clean background area for mercury. The monitoring staff planned a number of tests for the analyzers while at this location. Unfortunately a lamp failure on the second TEKRAN analyzer limited the work that could be completed. The data collected using the MAT and the TEKRAN analyzers is now in review and the results should be reported in the next quarter.

The final ambient monitoring project was a test of the gold traps for long duration mercury sampling. These gold traps are commercially prepared glass tubes filled with gold-coated sand. The tubes will trap mercury from air drawn through the tubes. At the analysis laboratory, the mercury is thermally desorbed from the gold and the mercury measured using an atomic fluorescence analyzer. The analysis follows the protocol in USEPA Method IO-5. The test was conducted by sampling the ambient air at the Nevin Fish Hatchery concurrent with the operation of the TEKRAN analyzers. The goal of the test was demonstrating the two methods produce compatible results. Wisconsin plans to use the gold traps in a simple sampling train for aircraft sampling during the 2002 sampling season.

Computer Resources

Currently, all our atmospheric and meteorological modeling has been performed on the DEC workstation. Recently, we acquired a Linux cluster (one master and two compute nodes) for use with mercury modeling. This cluster was bought by LADCO and will be used for PM and haze modeling as well. The cluster is installed and running well. Mike Majewski attended a Linux workshop last Spring and will administer the cluster. To date, the following models have been installed on the cluster: CAMX, REMSAD, CMAQ, and MM5.